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Electrical conductivity, impedance, and percolation behavior of carbon nanofiber and carbon nanotube containing gellan gum hydrogels

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Abstract

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Keywords

Biopolymers, carbon nanofiber, carbon nanotubes, composites, conductivity, fillers, fullerenes, gellan gum, hydrogels, impedance, polysaccharides, structure-property relationships

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

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Electrical conductivity, impedance and percolation behaviour of carbon nanofibre and carbon nanotube containing gellan gum hydrogels

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Abstract

The electrical impedance behaviour of gellan gum (GG), GG-carbon nanotube and GG-carbon nanofibre hydrogel composites is reported. It is demonstrated that the impedance behaviour of these gels can be modelled using a Warburg element in series with a resistor. Sonolysis (required to disperse the carbon fillers) does not affect gellan gum hydrogel electrical conductivity (1.2 ± 0.1 mS/cm), but has a detrimental effect on the gel's mechanical characteristics. It was found that the electrical conductivity (evaluated using impedance)

increases with increasing volume fraction of the carbon fillers and decreasing water content. For example, carbon nanotube containing hydrogels exhibited a 6-7 fold increase in electrical conductivity (to 7 ± 2 mS/cm) at water content of 82%. It is demonstrated that at water content of $95 \pm 2\%$ the electrical behavior of MWNT containing hydrogels transitions (percolates) from transport dominated by ions (due to gellan gum) to transport dominated by electrons (due to the carbon nanotube network).

1. Introduction:

Electrically conducting hydrogel materials have been studied for a wide range of applications such as strain sensors for soft robotics,^{1,2} stretchable conductors,³ foldable actuators^{4,5} and neural prosthetic interfaces.⁶ As non-ionic hydrogels are not natively electrically conductive, researchers have used various approaches to increase the electrical conductivity of hydrogels by adding salt,^{1,3} doping with strong acids,⁷ and incorporating conducting fillers such as conducting polymers like poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS).⁸⁻¹⁰

In addition, it is well-known that the swelling ratio (wet mass divided by dry mass) or water content of hydrogels has an important effect on the mechanical and electrical characteristics of hydrogels.¹¹ For example, it has been shown that the electrical conductivity of double network hydrogels incorporated with a conducting polymer (PEDOT) is inversely proportional to the swelling ratio.¹¹

The conductivity of ion (ionic liquid containing) gels and hydrogels has been evaluated using a wide variety of methods. They include alternating and direct current measurement

techniques such as electrical impedance, conductivity meters and 4-point probe methods.⁸⁻
^{10,12,13} There are a number of differences between these methods. For example, conductivity meters evaluate the impedance using an alternating current at a single frequency, whereas 4-point methods use a direct current, which is applied to the surface.

Most of the reported electrical conductivity values for conducting filler composite hydrogel materials are in the order of 1-2 mS/cm. For example, PEDOT:PSS composite hydrogels (water content 75-90%) exhibited values in the range 0.67 to 2.6 mS/cm depending on the conducting polymer content.^{9,10} Similar electrical conductivity values were obtained for hydrogels consisting of polyacrylate and a conducting polymer.^{12,14} Higher values (> 4.3 mS/cm) have been reported, but this usually requires different synthesis strategies,¹¹ or hydrogels solely consisting from conducting polymer, i.e. without a polymer matrix.¹⁵

Gellan gum (GG) is an anionic extracellular polysaccharide produced by a fermentation process of the bacterium *Pseudomonas elodea*.¹⁶ It is a hydrogel-forming biopolymer, commonly used in the food industry as a thickener.¹⁷ GG forms rigid gels by cross-linking with cations. It has been shown that divalent cations, such as magnesium and calcium, are more effective cross-linkers than monovalent cations.^{17,18} The application of GG as a material for tissue engineering is rapidly gaining attention.^{19,20} In addition, several groups (including ours) have shown that GG is an efficient dispersant for conducting carbon fillers such as carbon nanotubes and carbon nanofibres.²¹⁻²⁴

In this paper, we present the preparation and characterisation of conducting carbon filler containing GG hydrogels. Conducting carbon fillers such as single-walled (SWNTs) and multi-walled (MWNTs) carbon nanotubes and vapour grown carbon nanofibres (VGCNFs) are incorporated into hydrogels using sonication, followed by physical cross-linking with

Ca²⁺ ions. The gels are characterised using oscillatory rheology and electrical impedance analysis.

2. Experimental:

2.1. Dispersion preparation

Gellan gum (GG) solutions were prepared by dissolving dry GG powder (low acyl gellan gum, Gelzan, lot # 1I1443A), which was received as a gift from CP Kelco, in Milli-Q water (100 mL, ~80 °C, resistivity 18.2 MΩ cm), while stirring at ~800 r.p.m (IKA RW 20 digital). Composite dispersions of VGCNFs (Pyrograf Products, PR24-LHT, Batch info: PS 1345 Box 8, HT 170), MWNTs (Nanocyl S.A., Belgium, lot #090901) and SWNTs (Unidym Inc., USA, lot # P0261) in GG with carbon materials:GG weight ratios of 10:3, 10:3 and 10:4, respectively, were prepared using probe sonication with a digital sonicator horn (Branson Digital Sonifier). A power output of 6 W was utilised with a 0.5 s on/off pulsing cadence and a tapered microtip (Consonic, diameter 3.175 mm) placed 1 cm from the bottom of a glass vial (diameter 25 mm)

2.2. Gel preparation

Hydrogels were prepared such that the final concentration of GG was 0.5% w/v. Gellan gum hydrogels were prepared by cross-linking GG solutions or GG solutions which were subjected to sonolysis of up to 50 min by adding 5mM CaCl₂. For example, a sonicated gellan gum hydrogel is prepared by sonicating 5 mg/ml GG (0.5% w/v) for 50 min prior to cross-linking with Ca²⁺ ions (5 mM CaCl₂, 80 °C). The solutions were then poured into

plastic moulds and allowed to cool under controlled ambient conditions (21 °C, 45 % relative humidity).

Composite hydrogels were prepared by adding fresh GG powder to VGCNF, MWNT and SWNT dispersions (with stirring and heating at 80 °C until fully hydrated) to increase the GG concentration to 0.5% w/v, prior to cross-linking with Ca²⁺ ions (5 mM CaCl₂, 80 °C). For instance, a hydrogel containing 10 mg/ml of MWNT is prepared by sonicating MWNT (10 mg/ml) for 30 min in 3 mg/ml of GG, after which fresh GG powder is added to bring the total GG concentration to 5 mg/ml (0.5% w/v). The dispersions were poured into plastic moulds and allowed to cool under controlled ambient conditions (21 °C, 45 % relative humidity using a Thermoline Scientific temperature/humidity chamber). Regardless of the amount of carbon filler, the same proportion of GG was subjected to sonication. It should be noted that the duration of sonication depends on amount and type of conducting filler, as it is easier to disperse equivalent amounts of VGCNFs compared to MWNT as described in the Results and Discussion section.

Hydrogels with water content from 0-100% were prepared by selectively removing water under controlled ambient conditions using the temperature/humidity chamber. Water content was determined using weight measurement.

2.3. Characterisation

Rheological analysis was carried out with an Anton Paar Physica MCR 301 Digital Rheometer (parallel plate tool, 15 mm diameter) at 21 °C, with the aid of a Peltier

temperature controlled bottom plate system. Gels were poured into a mould with dimensions of 10 mm height, 16 mm diameter. Strain amplitude sweep experiments were carried out at constant frequency of 10 Hz and oscillating strain varying between 0.01 % and 10 %.

The electrical impedance behaviour of gel samples was obtained for frequencies between 1 Hz and 100 kHz using a custom-designed instrument and sample compartment (Figure 1). The sample compartment contains gels which were moulded into a rectangular shape with a width of 1 cm, height 1 cm and length up to 2.5 cm. Reticulated vitreous carbon (RVC, ERG Aerospace) was incorporated into the gels to provide gel-electrode contact, as seen in Figure 1C. Impedance analysis was performed by applying a 1 V peak voltage (alternating current signal) using a waveform generator (Agilent U2761A), across the circuit consisting of a known resistor (R_k , 10 k Ω) and the gel sample. The impedance was obtained by measuring the voltage drop across the known resistor with an oscilloscope (Agilent U2701A).

2.4. Statistical treatment

The reported results are averages of the values obtained. Reported numerical errors and graphical error bars are given as ± 1 standard deviation (SD). Data and outliers were rejected either when instrumental error was known to have occurred, or if data failed a Q-test with a confidence interval $\geq 95\%$.

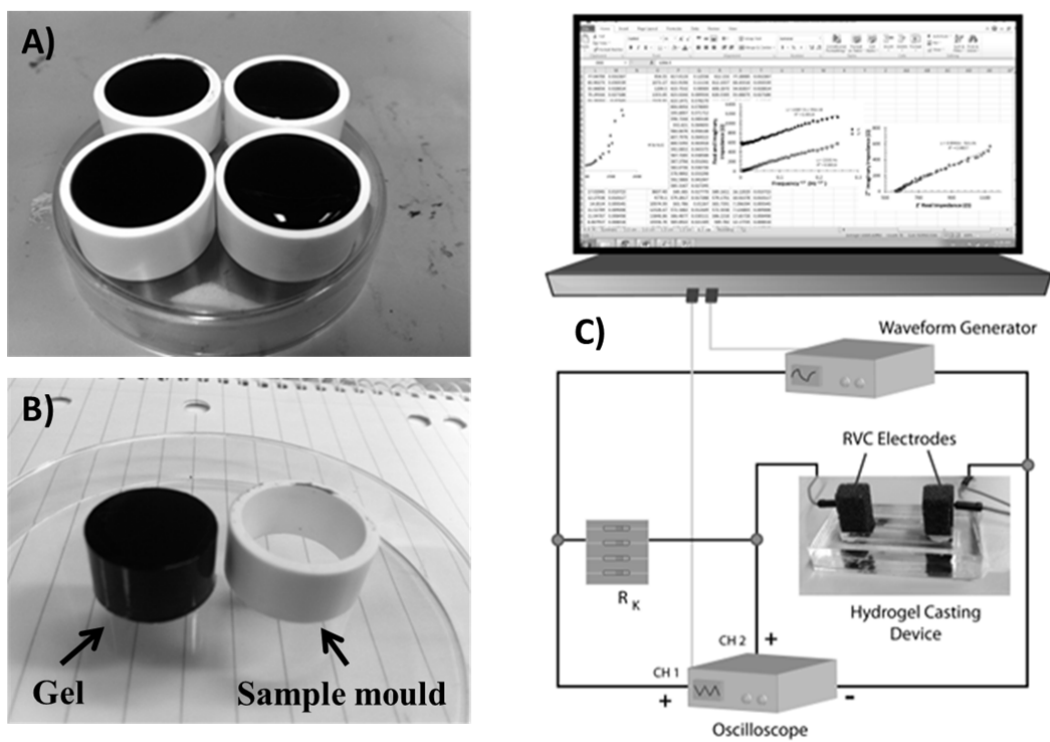


Figure 1. A) and B) Photographs of typical hydrogel samples (height 10 mm, diameter 16 mm). C) Schematic of the custom-built electrical impedance analyser.

3. Results and Discussion

3.1. Impedance and electrical conductivity of gellan gum hydrogels

Electrical impedance analysis on gellan gum hydrogels, contacted with porous electrodes, was carried out using a custom-built instrument (Figure 1C). The impedance measured in this manner provides information about the frequency dependent behaviour of the charge carriers inside the gels. This method is different from other commonly employed techniques such as

an electrochemical impedance spectroscopy approach (evaluates the interfacial behaviour of charge carriers), 4-point probe (applies a direct current usually to the surface of the material) and conductivity meters (applies a single alternating frequency). Figure 2A shows a Bode plot of a typical GG hydrogel cross-linked with 5 mM Ca²⁺. The impedance magnitude ($|Z|$) decreases with increasing frequencies and become independent of frequency above 1 kHz.

The corresponding Nyquist plot (Figure 2B) displays a linear relation between the real (Z') and imaginary (Z'') components of the impedance. At the intercept with the x-axis, the impedance is purely real ($Z'' = 0$) and the Z' value represents a resistance. The slope in the Nyquist plot is ~ 1 , suggesting a 45° constant phase shift between real and imaginary components of the impedance. This can also be recognised from a log-log version of the Bode plot, i.e. slope of $-1/2$ in the low frequency region (data not shown). This suggests that the hydrogel is behaving like a Warburg diffusion element (Z_W), in series with a resistor (R_I).²⁵

Under this model, Z' and Z'' are inversely proportional to the square root of the frequency (ω)²⁵,

$$Z' = R_I + \frac{\mu}{\sqrt{\omega}}, \quad (1)$$

$$Z'' = \frac{\mu}{\sqrt{\omega}}, \quad (2)$$

where μ is the Warburg coefficient. This dependence is unique to the Warburg impedance and is generally referred to as the Warburg plot (Figure 2C). A fit of this data to equations 1 and 2 revealed $R_I = 554 \pm 3 \Omega$ and $\mu = 2410 \pm 120 \Omega/s^{1/2}$. R_I and μ can also be determined by

equivalent circuit modelling (Figure 2A), which yielded $R_l = 672 \pm 3 \Omega$ and $\mu = 2200 \pm 10 \Omega/s^{1/2}$. The magnitude of R_l and μ are influenced by the polymer and charge carrier concentrations. For example, μ was found to be inversely proportional to Ca^{2+} concentration (data not shown). In the remainder of this paper, the values quoted for R_l and μ are determined using equivalent circuit modelling.

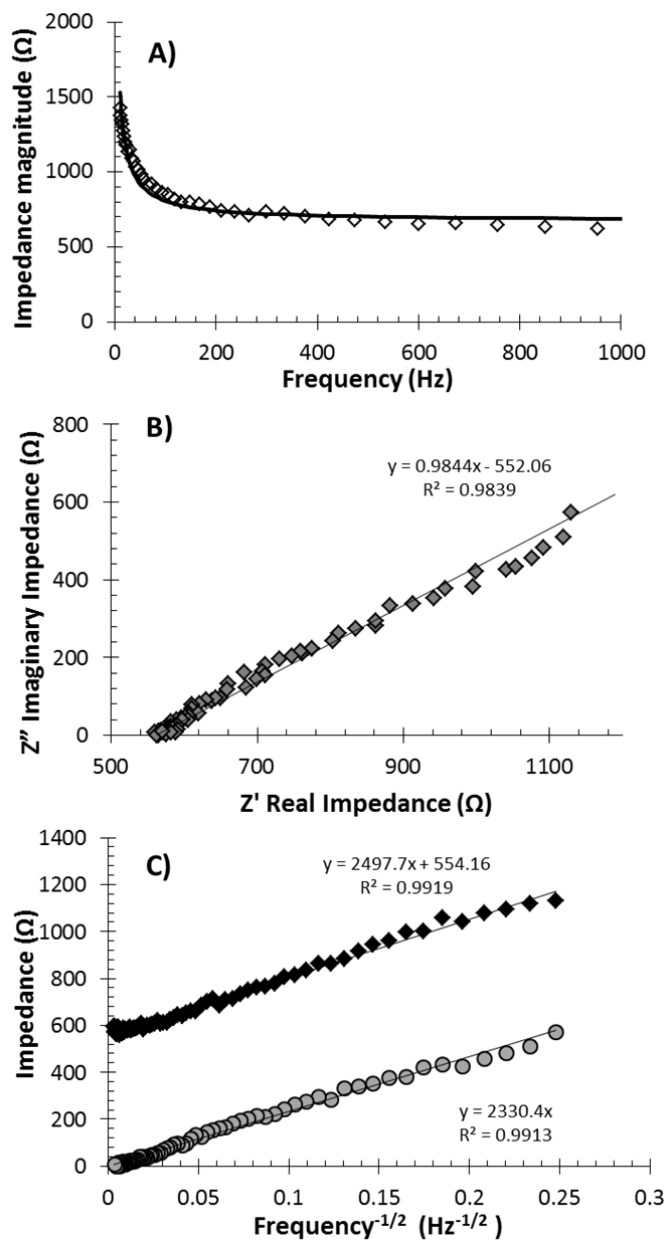


Figure 2. Electrical impedance analysis of a typical gellan gum hydrogel (0.5 % w/v, cross-linked with 5 mM CaCl_2) of dimensions 0.5 cm (l) x 1 cm (w) x 1 cm (h). A) Bode plot, B) Nyquist plot and C) Warburg plot. The solid line in A is a 2 parameter fit of data to an equivalent circuit model consisting of a Warburg element in series with a resistor, while the solid line in B is a straight line fit and in C is a fit to equation 1.

The impedance values measured in this manner include a contact resistance, R_C , due to the interface between gel and electrodes (porous reticulated vitreous carbon, RVC). It was

observed that the impedance magnitude (at any given frequency) increased with increasing gel length (Figure 3A). Equivalent circuit modelling revealed that R_I was linearly proportional to gel length (Figure 3B), while μ was invariant with length (Figure 3C). Hence, the increase of R_I is directly related to the amount of gel material, which increases with length. This provides us with a method to correct the R_I value due to the presence of electrode-hydrogel contact resistance by realising that R_I vs l should obey,

$$R_I = \frac{l}{\sigma A_C} + R_C, \quad (3)$$

where A_C is the gel's cross-sectional area and σ is the gel's electrical conductivity (at high frequencies). Fitting equation 3 to the data shown in Figure 3B yielded $\sigma = 1.2 \pm 0.1$ mS/cm and a contact resistance value of $176 \pm 75 \Omega$.

One of the aims of this work is to investigate the electrical characteristics (including conductivity) of conducting carbon filler containing hydrogels, which requires the use of sonolysis. Hence, it is important to determine the effect of sonication on the gel's electrical and mechanical characteristics prior to incorporation of the conducting fillers such as carbon nanotubes and carbon nanofibres.

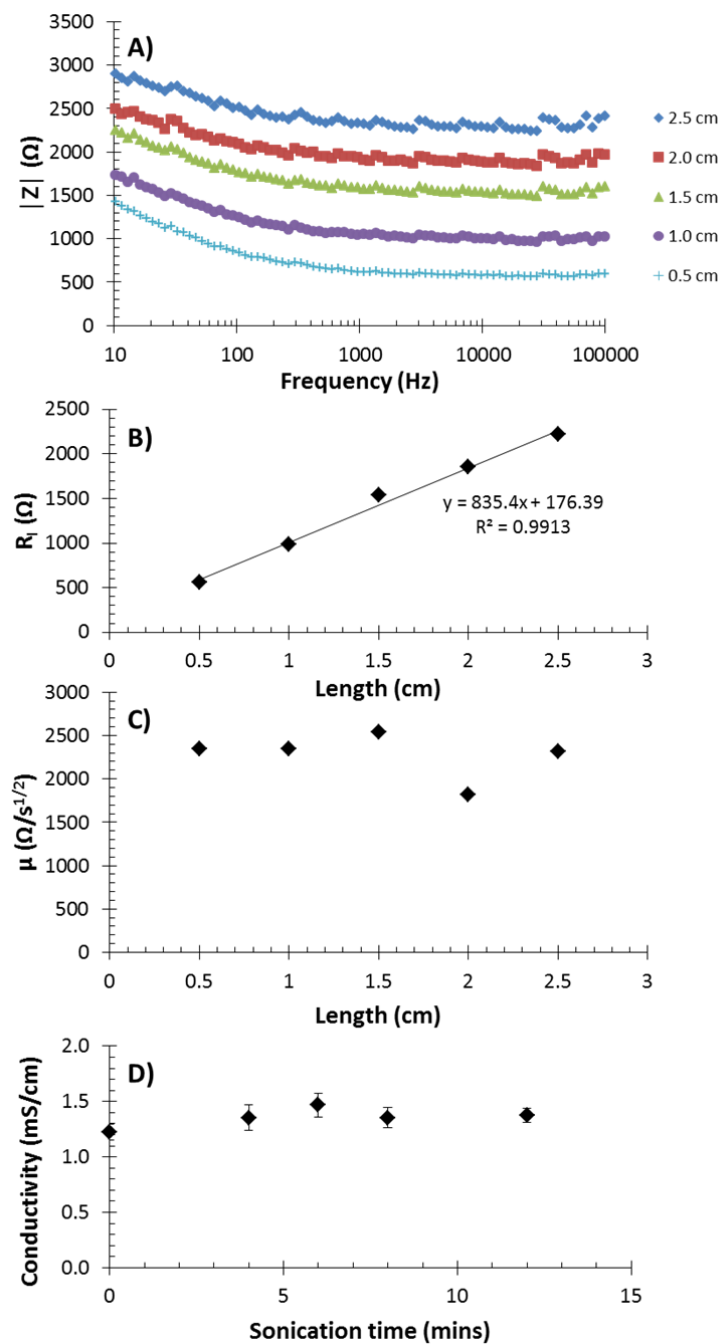


Figure 3. A) Typical impedance magnitude ($|Z|$) of GG hydrogels of varying length. B) Typical resistance (R_l) as a function of gel length. C) Typical Warburg coefficient (μ) values as a function of gel length. D) Electrical conductivity of GG hydrogels (0.5% w/v, cross-linked with Ca²⁺) as a function of sonication time, calculated from impedance analysis. Straight line in B) is a linear fit to equation 3. μ and R_l are obtained from equivalent circuit modelling of data shown in A).

The effect of sonolysis was assessed by preparing gellan gum hydrogels which were subjected to probe sonication of up to 40 mins. Impedance analysis was used to evaluate the electrical conductivity, as described in the previous section. Figure 3 D shows that the gel electrical behaviour is not affected by sonication.

The decreasing trends observed in Figure 4 are a direct result of the shortening of the polymer chains due to the process of horn sonolysis.²⁶ During the sonication process, cavities are created which leads to polymer chains experiencing large shear forces.²⁷ This results in a considerable reduction in the average chain length.²⁸ Cross-linked gels formed from sonicated GG solutions are less rigid and flow more easily with an applied shear strain; as evident from the reduction in storage modulus with increasing sonication time (Figure 4).

Composite hydrogels were prepared by dispersing 1 mg/ml of either SWNTs, MWNTs or VGCNFs into GG solutions with the aid of low energy sonolysis. The GG concentration was adjusted such that the carbon material volume fraction for all three materials was about 0.09%. The density values of SWNT (1.50 g/cm³), MWNT (2.15 g/cm³), VGCNF (1.95 g/cm³) and GG (1.3 g/cm³) were used to convert mass fraction into volume fraction.²¹

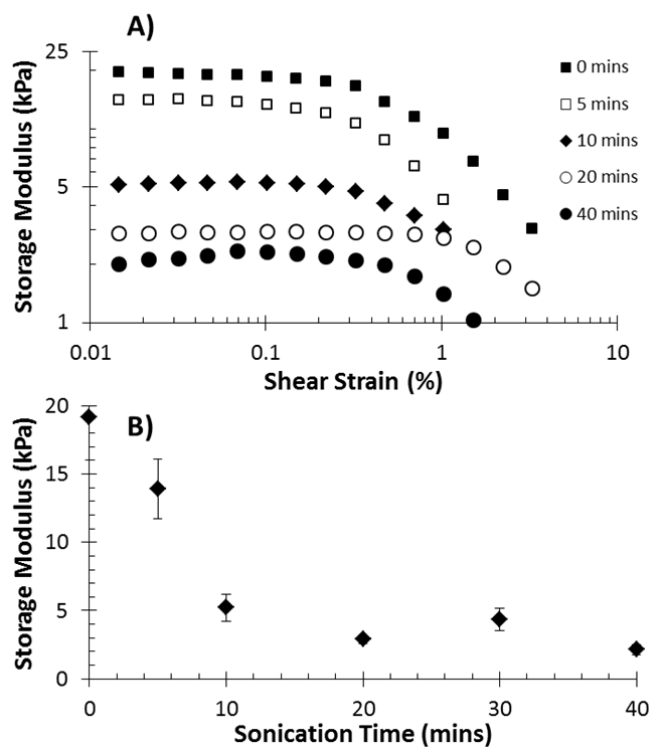


Figure 4. A) Storage modulus as a function of shear strain for GG hydrogels (0.5% w/v, cross-linked with 5 mM Ca²⁺) subjected to sonication. B) Storage modulus in the LVE region as a function of sonication time.

Composite hydrogels were prepared by dispersing 1 mg/ml of either SWNTs, MWNTs or VGCNFs into GG solutions with the aid of low energy sonolysis. The GG concentration was adjusted such that the carbon material volume fraction for all three materials was about 0.09%. The density values of SWNT (1.50 g/cm³), MWNT (2.15 g/cm³), VGCNF (1.95 g/cm³) and GG (1.3 g/cm³) were used to convert mass fraction into volume fraction.²¹

It is well-known that SWNTs are difficult to disperse, which is evident from the 120 ± 10 min required to disperse 10 mg in GG solution (10 mL). In contrast, equivalent amounts of MWNTs and VGCNFs took a lot less time (energy) to disperse, 12 ± 4 min and 2 ± 0.5 min,

respectively. Impedance analysis showed that the gel electrical conductivity is similar for all 3 types of conducting filler ($\sigma \approx 1.2$ mS/cm), despite the large differences in the conductivity of these materials in thin film form, i.e. 110 ± 15 S/cm (SWNT), 50 ± 5 S/cm (MWNT) and 35 ± 2 S/cm (VGCNF).

This suggests that (in the hydrogels) the carbon-material volume fraction (0.09%) is too low to contribute to the conduction mechanism. We aimed to address this using two approaches (discussed in the next 2 sections), (i) increasing the carbon volume fraction (which in turn requires increasing the sonication time), and (ii) decreasing water content.

However, increasing the SWNT concentration beyond 1 mg/ml was not practical due to the already large sonication times required to achieve a complete dispersion at that concentration. Therefore, all further experiments involved VGCNFs and MWNTs.

3.2. Effect of increasing carbon filler volume fraction

All hydrogels were prepared with a GG concentration of 5 mg/mL and water content > 98.5%. Dispersing MWNT at a concentration of 10 mg/mL in GG required 30 min of sonication. It is shown in Figure 4 that this length of sonolysis results in significant weakening of the gels. Hence, it was not possible to form MWNT containing hydrogels by simply cross-linking the dispersion. Instead, fresh GG powder was added to the dispersions. These dispersions were cross-linked using Ca^{2+} ions and cast in plastic moulds while hot (~ 80 °C), to form rigid gels upon cooling to room temperature (21 °C).

The Bode plots for the MWNT hydrogels are shown in Figure 5A. It is clear that increasing the MWNT volume fraction results in a decrease in the magnitude at all frequencies. This indicates that the presence of MWNT is improving the electrical characteristics of the gels.

VGCNF gels were prepared using a similar approach as the MWNT gels, i.e. GG concentration is always fixed at 5 mg/mL. As VGCNF required less sonolysis compared to the MWNT, it was possible to prepare hydrogels with higher volume fractions compared to the MWNT. Dispersing 17.5 mg/mL of VGCNF required only 12 min of sonication. This difference allowed for the preparation of gels with volume fraction of up to 0.89%. Regardless of the volume fraction, the same proportion of GG was subjected to sonication.

The Bode plots for the VGCNF hydrogels (Figure 5B) exhibit the same trends as shown for the MWNT gels, i.e. the impedance magnitude decreases with increasing VGCNF volume fraction.

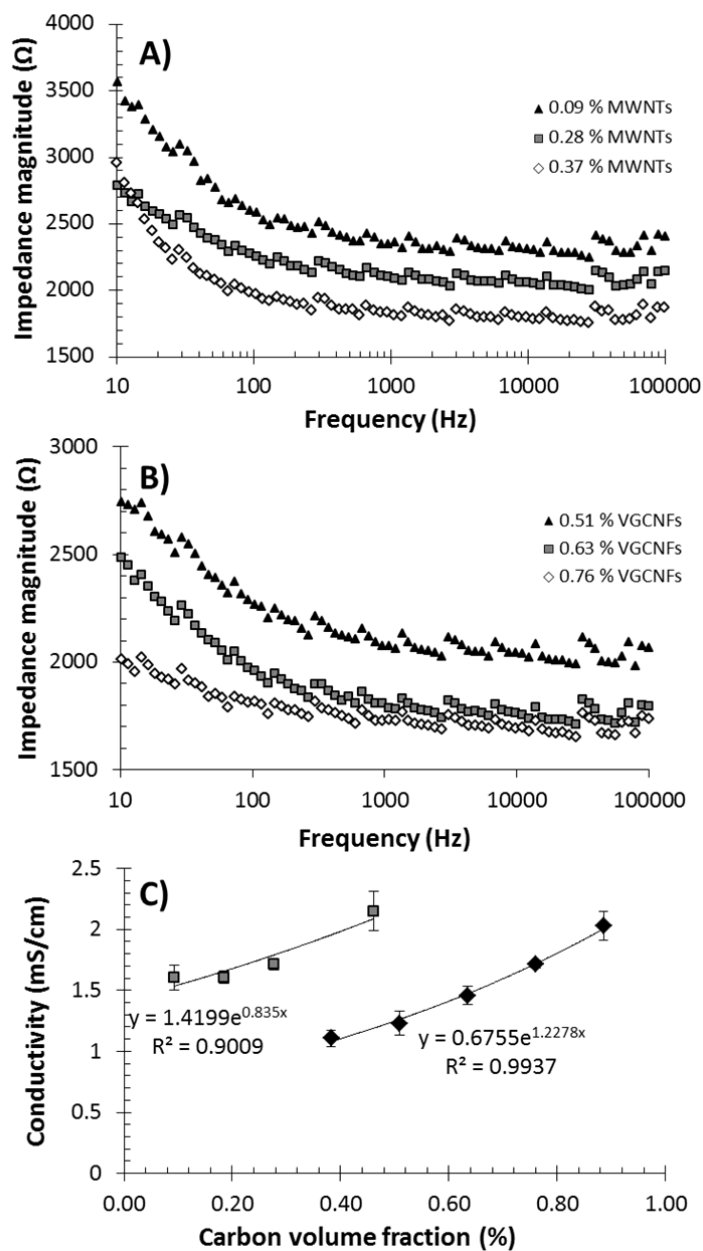


Figure 5. A) and B) Typical impedance magnitude ($|Z|$) of MWNT and VGCNF hydrogels (length = 1 cm) with different carbon material volume fractions, respectively. C) Electrical conductivity as a function of carbon filler volume fraction for GG hydrogels (0.5% w/v, cross-linked with Ca^{2+}). Squares and diamonds indicate MWNT and VGCNF, respectively. Lines are fits to the data.

A comparison between the two different types of carbon material containing gels (water content > 98.5%) leads to the following observations: (i) VGCNFs require less sonolysis to

disperse than MWNTs, and (ii) MWNTs require a lower volume fraction to influence the electrical conductivity. For example, the volume fractions required to reach an electrical conductivity value of 2.1 ± 0.4 mS/cm is about 0.89% for VGCNF, but only 0.41% for MWNTs. This could be attributed to the higher intrinsic electrical conductivity of MWNTs over VGCNFs.

This approach is clearly limited by the amount of water (98.5%) present in these gels. It was not possible to increase the carbon filler volume fraction beyond 0.89% (and thereby decrease the water content) due to the disperse-ability of the conducting fillers and the sonication method. Therefore, in the following section the effect of reducing water content on the electrical behaviour of the gels was investigated.

3.3. Effect of decreasing water content

The hydrogels were prepared at the highest possible carbon filler concentration with water content $> 98.5\%$, i.e. MWNT and VGCNF volume fractions of 0.41% and 0.89%, respectively, as outlined in the previous section. These gels (starting weight ≈ 4.2 g) were then placed in a temperature-humidity chamber and their water content was selectively reduced under controlled circumstances at a rate of 0.43 ± 0.01 g/hour. This experiment (which can be seen as de-swelling) allows us to maintain accurate knowledge of the water, polymer and conducting filler contents in our gels.

The Bode plots of MWNT gels at different water contents are shown in Figure 6. At 98% the Bode plot shows a dependence of impedance magnitude on frequency similar to those shown in Figures 3A and 5A. It shows a clear frequency-dependent region for frequencies below 1

kHz, and we have shown that this transport behavior is indicative of a Warburg element in series with a resistor. However, as the water content decreases, the frequency dependence at lower frequencies disappears. It is clear that at 94.5% water content, the Bode plot is indicative of a resistor, i.e. transport dominated by electrons. Equivalent circuit modeling revealed that the Warburg coefficient values decreased from $1400 \Omega/s^{1/2}$ at WC = 98% to $19 \Omega/s^{1/2}$ at WC = 94.5% (see Figure 7A). These could suggest that a percolative MWNT network is formed, which is further explored below.

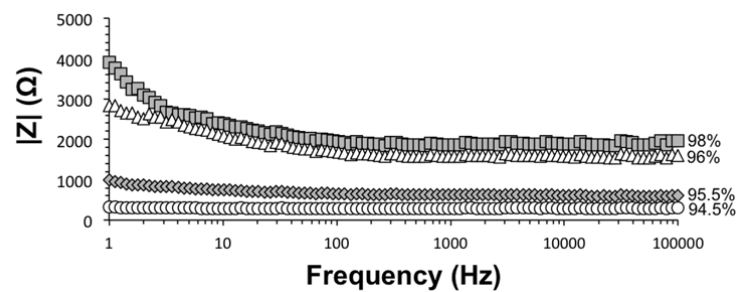


Figure 6 Typical Bode plots for MWNT containing hydrogels at water contents of 98.0%, 96.0%, 95.5% and 94.4%.

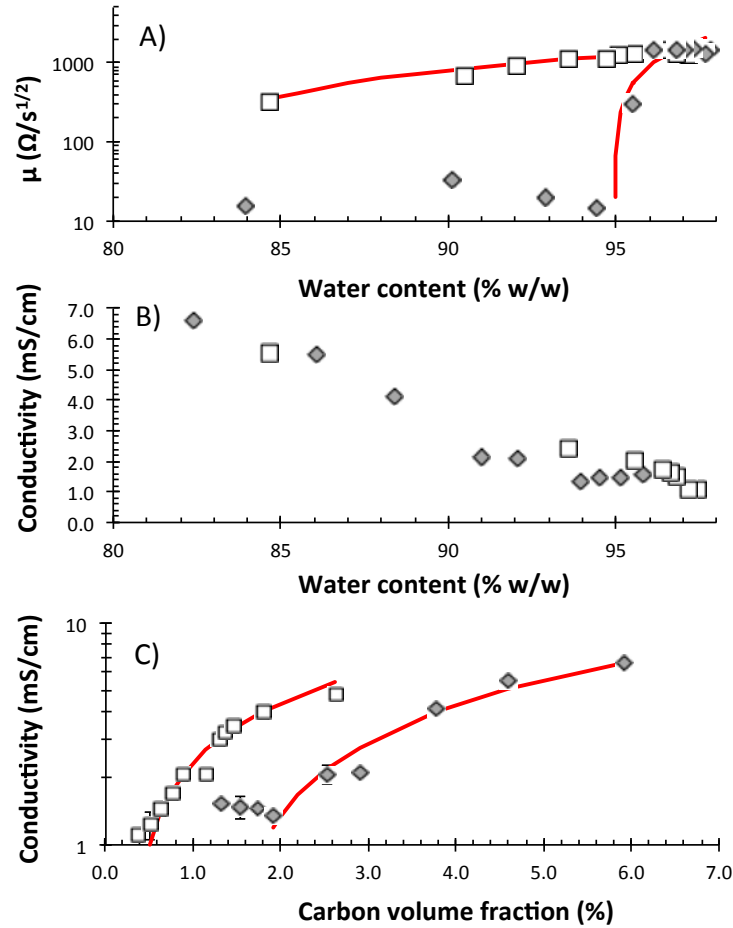


Figure 7 A) Typical Warburg coefficient (μ) values as a function of water content for MWNT (diamonds) and VGCNF (squares) containing hydrogels. The solid lines are three-parameter fits of the Warburg coefficient to equation 4. B) Electrical conductivity as a function of water content for MWNT (diamonds) and VGCNF (squares) containing hydrogels. C) Electrical conductivity as a function of carbon filler volume fraction for MWNT (diamonds) and VGCNF (squares) containing hydrogels. The solid lines are three parameter fits to equation 5.

Our analysis of conducting filler network formation was based on Warburg coefficient data for the following reason. During the de-swelling experiment, gels undergo a dimensional change as a result of water loss. Figure 3B shows that the resistance is dependent on gel dimension; whereas Figure 3C shows that the Warburg coefficient is not.

Figure 7A shows that the dependence of the Warburg coefficient on water content for MWNT containing gels undergoes a sharp transition around WC = 95%. This transition

identifies the WC point at which the electrical behaviour of the gels becomes dominated by electrons, i.e. formation of a conducting filler network in the hydrogel. This trend is similar to the well-known scaling behaviour of electrical conductivity with conducting filler mass fraction in composite materials. The composite materials become electrically conducting at the threshold concentration where a percolative network is formed. This behaviour is traditionally fitted using the statistical percolation model.^{29,30} Our data could be fitted using a similar model:

$$\mu = \mu_0 (WC - WC_p)^t + C, \quad (4)$$

where μ_0 is a scaling factor, WC_p is the percolation threshold in terms of water content, C is a constant, and t is the exponent. A fit of the data for MWNT gels (Figure 7A) resulted in the following values, $\mu_0 = 420 \pm 180 \text{ } \Omega/\text{s}^{1/2}$, $WC_p = 95 \pm 2\%$, $t = 1.5 \pm 0.6$, and $C = 20 \pm 8 \text{ } \Omega/\text{s}^{1/2}$, respectively.

In contrast to the MWNT gels, the VGCNF containing gels exhibited a more gradual reduction in Warburg coefficient. For example, μ decreased from $1400 \text{ } \Omega/\text{s}^{1/2}$ at WC = 98% to $325 \text{ } \Omega/\text{s}^{1/2}$ at WC = 85%, with a further reduction to $3 \text{ } \Omega/\text{s}^{1/2}$ at WC = 60%. A fit of this data to equation 4 revealed the following values, $\mu_0 = 88 \pm 20 \text{ } \Omega/\text{s}^{1/2}$, $WC_p = 81 \pm 2\%$, $t = 1.0 \pm 0.4$, and $C = 3 \pm 1 \text{ } \Omega/\text{s}^{1/2}$, respectively.

The electrical conductivity of the gels as a function of water content was determined using R_l values (as determined by equivalent circuit modeling), the gel's dimension and equation 3. Figure 7B shows that the conductivity of the MWNT and VGCNF gels increased with decreasing water content (Figure 7B). For example, at WC = 82% the MWNT containing gel yielded an electrical conductivity value of 7 ± 1 mS/cm. Similar values were obtained for the VGCNF containing gels.

The combined electrical conductivity data for the effects of increasing carbon filler (Figures 5 C) and decreasing water (Figure 7 B) is shown in Figure 7 C and was fitted using the statistical percolation model:

$$\sigma = \sigma_0 (\varphi - \varphi_p)^t, \quad (5)$$

where σ_0 is a scaling factor, φ is the carbon filler volume fraction, φ_p is the percolation threshold in terms of carbon filler volume fraction and t is the exponent. The resulting t values of the MWNT ($t = 0.8 \pm 0.3$) and VGCNF ($t = 0.7 \pm 0.3$) containing gels are lower than the predicted scaling values for in two and three dimensions, i.e. $t = 1.3$ and $t = 2$, respectively.

Conclusions

The mechanical and electrical characteristics of gellan gum, carbon nanotube-gellan gum and vapour-grown carbon nanofibre hydrogels has been investigated. The electrical

characteristics of these hydrogels were assessed using a custom-built impedance analyser. Our analysis revealed that the impedance behaviour of these gels could be modelled using a Warburg diffusion element in series with a resistor. These resistor values were used to calculate the electrical conductivity after correcting for electrode-sample contact resistance.

Sonolysis had a detrimental effect on the mechanical characteristics, as measured using the shear modulus. For example, subjecting a gellan gum solution to 40 minutes of horn sonication prior to gelation resulted in a decrease in shear modulus from 19.2 ± 3.1 kPa to 2.2 ± 0.4 kPa. In contrast, it was observed that sonolysis did not affect the electrical conductivity of the gellan gum hydrogels (1.2 ± 0.1 mS/cm).

Incorporating MWNT and VGCNF through addition of more filler was found to result in a modest enhancement of the electrical conductivity. Larger increases in conductivity could be obtained by selectively removing water content.

Impedance analysis was used to show that MWNT containing hydrogels undergo a sharp transition from transport dominated by ions (due to gellan gum) to transport dominated by electrons (due to conducting fillers). For example, percolation analysis showed that the MWNT form a percolative network within the hydrogels at water content of $95 \pm 2\%$. MWNT containing gels exhibited an electrical conductivity of 7 ± 1 mS/cm at water content of 82%.

This paper contributes to the development and characterisation of electrically conducting hydrogel materials.

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